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Indium Alloy as Cadmium Brush Plating Replacement

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Prescribed by ANSI Std Z39-18

Project Details

- **Second Year of Effort**
- **Numerous Agencies / Companies Involved (partial list)**
  - Air Force Research Laboratory (AFRL)
  - Air Force Depots
  - NAVSEA (Naval Avionics Support Equipment Appraisal)
  - Concurrent Technologies Corporation *(CTC)*
  - Boeing
  - Matco Associates
  - Harris Consulting

Problem Statement

- Cadmium (Cd) plating is used on steel mating surfaces on a Department of Defense (DoD) Weapon System
  - Federal regulations of Cd have increased to protect human health and the environment
  - Rate of phase-out and cost have also increased

- Maintenance, repair, and overhaul operations of a component of the same weapon system have recently been transitioned to a different DoD facility
  - New DoD facility had previously eliminated Cd plating
  - DoD facility requested the United States Air Force (USAF) for replacement coating in the weapon's component

Conduct Electricity During Service

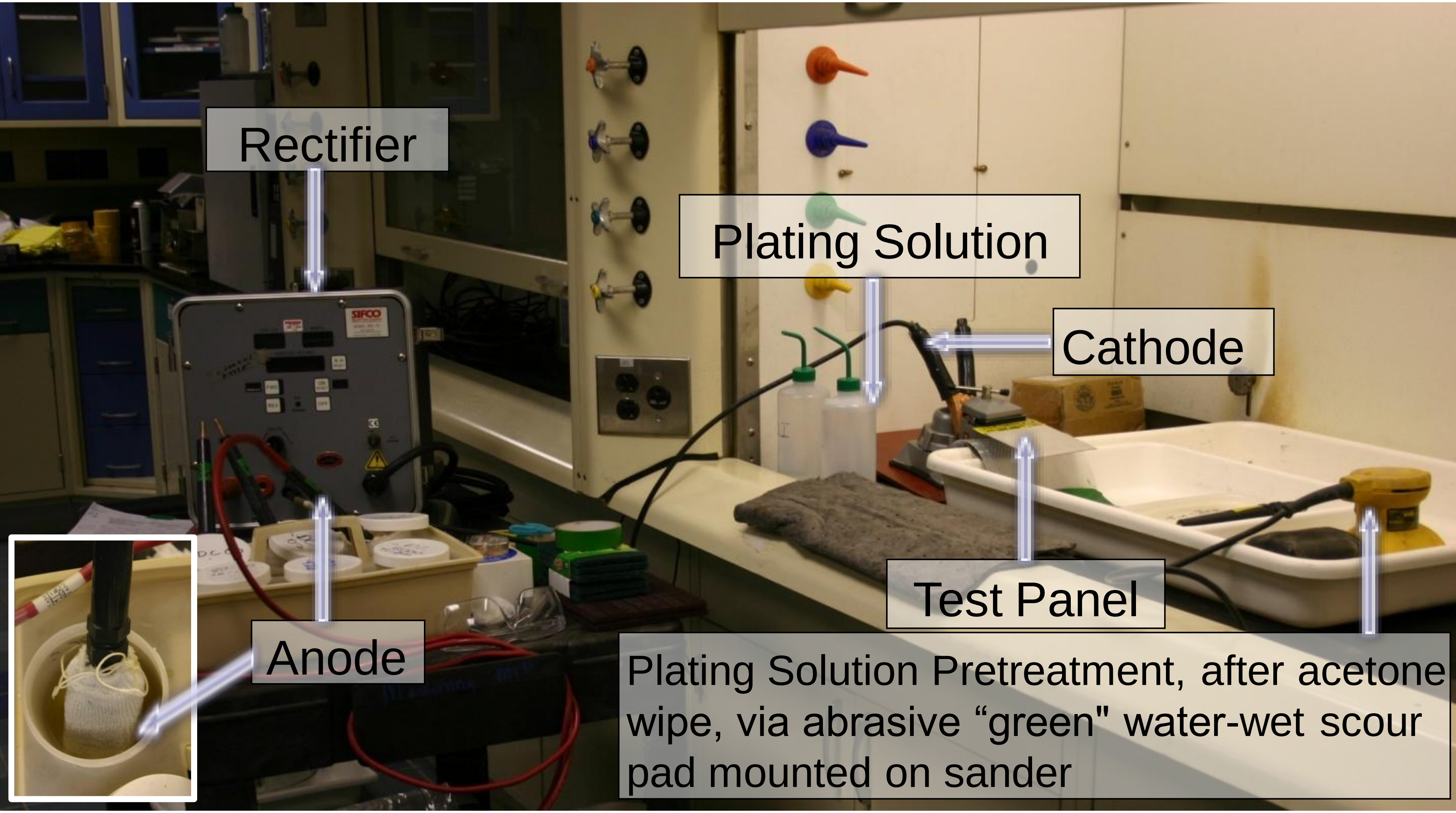
Mating Surfaces Must Remain Conductive

- Mating surfaces have dimensional tolerances
- Iron oxide is insulating and expands part volume
- Cd oxide is semi-conductive and non-voluminous

Objectives

- Identify replacement chemicals and required equipment for processing at DoD facility
- Investigate replacement repair plating process
- Define the process and testing criteria for alternatives
- Perform optimization testing on candidate coatings
- Recommend the process to be implemented after passing the demonstration / validation testing

Example Brush Plating Set-up



Dip anode in chemical; supplement from squirt bottle

Processing & Performance Replacement Requirements

- Meet SAE-AMS-QQ-P-416, Type I Class 2 Specification
  - No chromate conversion coating
  - 0.3 to 0.5 mils coating thickness
- Process the part coating within the repair production period
- Be compatible with DoD facility and worker capability
- Preserve the dimensional tolerance for the mating parts
- Sacrificially protect mild steel from corrosion
- Comparable or lower electrical resistivity than Cd during the service life
- Negligible change in volume between as-plated and end of service life (similar to Cd).

Eliminate Cd, Pb (and Nickel [Ni]?) Alternative (Alts)

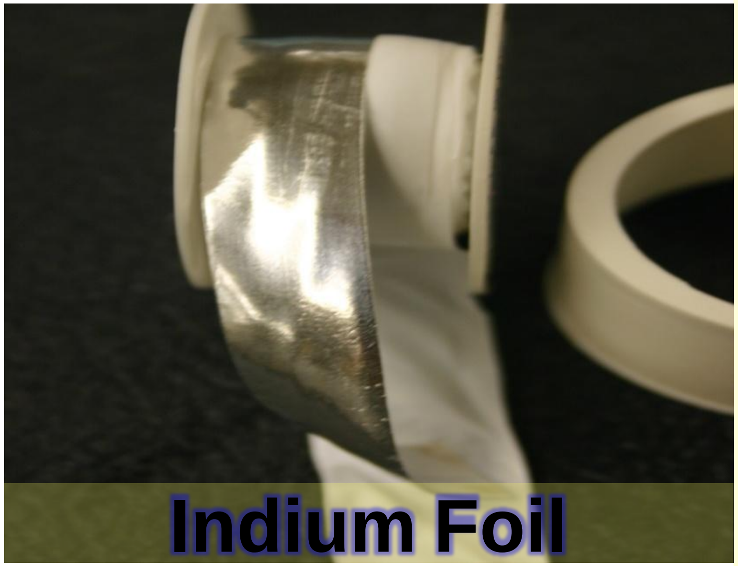
1. Aluminum
2. ~~Cadmium-titanium~~
3. Zinc
4. ~~Lead~~
5. ~~Zinc-cadmium~~
6. Nickel X?
7. Zinc-nickel X?
8. ~~Nickel-cadmium~~
9. Tin
10. ~~Tin-cadmium~~
11. Tin-nickel X?
12. Tin-zinc
13. Acrylic X?*
14. Epoxy X?*
15. Fluorocarbons X?*
16. Nylon X?*
17. Polyester X?*
18. Polyurethane X?*

* Organic coatings are unknown to be sacrificial sufficiently, when applied at 0.5 mils or less

Remaining Alts. per QQ-P-416

Alternative	Notes
~~1. Aluminum~~	Sacrifices to protect steel, converting to an alumina, which is an electrical insulator
~~2. Zinc~~	Also sacrificial to protect mild steel from corrosion; zinc oxide is 10X to 100X more electrically insulating than cadmium oxide
~~3. Tin~~	Plated tin is sacrificial to protect mild steel in seawater, but tin oxide is 10X more electrically insulating than cadmium oxide
4. Tin-zinc	Known to be sacrificial to protect mild steel, but its oxides’ electrical resistivity is unknown and needs to be tested

Could Indium / Indium Alloy be an Alternative?



- ✓ Not considered hazardous
- ✓ Commercial brush plating products can plate indium within thickness tolerances
- ✓ Sacrificial to mild steel (in sea water) and its couple to mild steel produces a potential <0.15 volts
- ✓ Electrically conductive, similar to Cd
- – Metal “cold welds” to itself / <u>Alloy Avoids “cold weld” issue</u>
- – Metal subject to halide attack / Alloy unknown to halide attack

Indium in a Galvanic Series

Lower Number is More Anodic

Active (Anodic)

1. Magnesium
2. Manganese
3. Zinc (plated)
4. Aluminum
5. Cadmium (plated)
6. **Indium**
7. Tin (plated)
8. Steel 1010
9. Iron (cast)
10. Copper (plated)
11. Nickel (plated)
12. Cobalt
13. Bismuth
14. Tungsten
15. Titanium
16. Silver
17. Gold
18. Graphite

Noble (Less Anodic)

MIL-STD-889; Series for Seawater

Replacements Down-selection

Key Requirements	Candidate Cd Plating Replacement							
Processing	Al	Zn	Ni	Sn	Zn-Ni	Sn-Ni	Sn-Zn	Sn-In
Meet Environmental Health and Safety (EHS) Standards	P	P	?/F	P	?/F	?/F	P	P
Fits within Overhaul Schedule	?	P	P	P	P	P	P	P
Fits with Worker Capability	?	P	P	P	P	P	P	P
Performance								
Coating Thickness	P	P	P	P	P	P	P	P
Adhesion to substrate	P	P	P	P	P	P	P	P
Contact Impedance	F	F	F	F	?	?	?	?
Expansion of Corrosion Products	F	F	F	P	?	?	P	?
Sacrificial Corrosion Protection	P	P	F	P	?	?	P	P
Whisker Growth (FOR INFO)	?	F	P	F	P	P	?	?

Al = Aluminum; In = Indium; Ni = Nickel; Sn = Tin; Zn = Zinc.
“P” = Pass; “F” = Fail; “?” = Unknown; “?/F” = Questionable Future.

Select Commercial Chemistries

Alternatives	Notes
1. Tin-zinc	Known to be sacrificial to protect mild steel, (but its oxides' electrical resistivity is unknown and needs to be tested). Prior work encountered processing inconsistency for target metal alloy composition.
2. Tin-indium	Sacrificial to mild steel (in seawater) and electrically conductive, similar to Cd; avoids "cold weld" issue. Possibility of halide attack is unknown. Processing inconsistency similar to tin-zinc is a concern.
Contingency	**Notes**
3. Zinc-nickel	Known to be sacrificial to protect mild steel when its nickel content is <25-30% by weight; its oxides' electrical resistivity is a concern and needs to be tested. Possible worker health and safety concern.

Alts. Chosen for Testing

Coating Round 1	Composition (nominal)	Coating Round 2	Composition (nominal)
Cd	100% Cd		100% Cd
Sn-Zn @ 7 volts(1)	90% Sn, 10% Zn		
Sn-Zn @ 12 volts (2)	70% Sn, 30% Zn	Sn-Zn @ 12 volts (2)	70% Sn, 30% Zn
Sn-In (1)	80% Sn, 20% In		
Sn-In (2)	90% Sn, 10% In		
In-Sn (3)	65% In, 35% Sn	In-Sn	70% In, 30% Sn
Zn-Ni (dip plated)	82% Zn, 18% Ni	Zn-Ni (brush plated)	85% Zn, 15% Ni

Electrical Resistance

Electrical Isolation (Kapton® Tape)

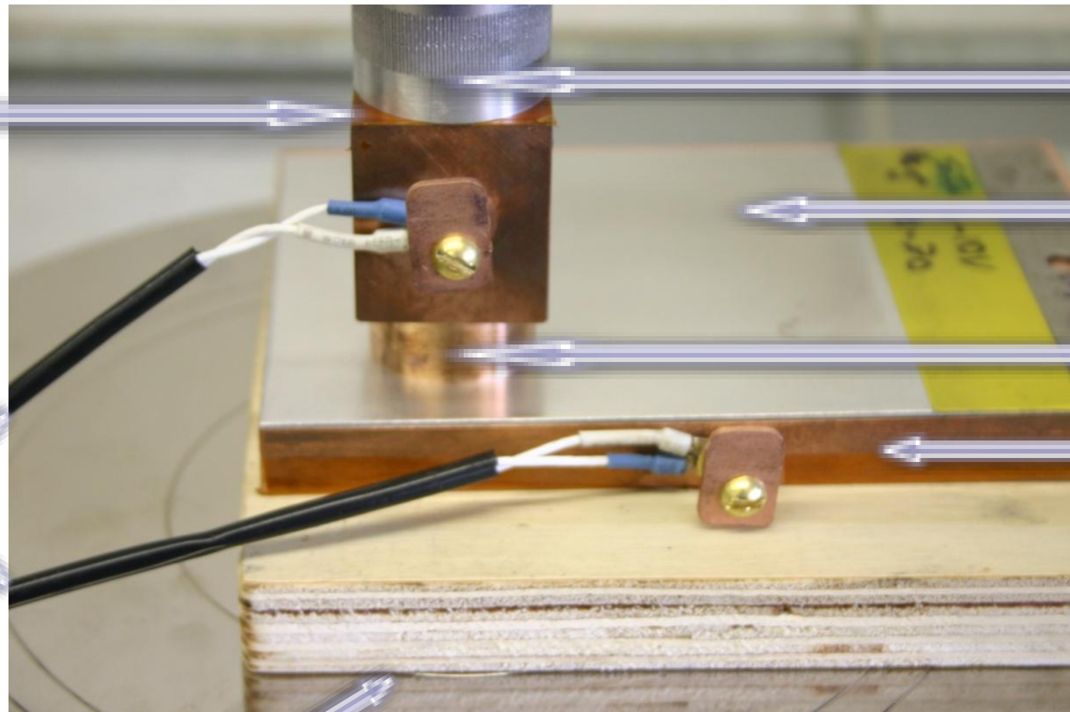
Load (200-pounds/inch^2)

Panel

Upper Electrode (1-inch^2 Area)

Lower Electrode (= Panel Area)

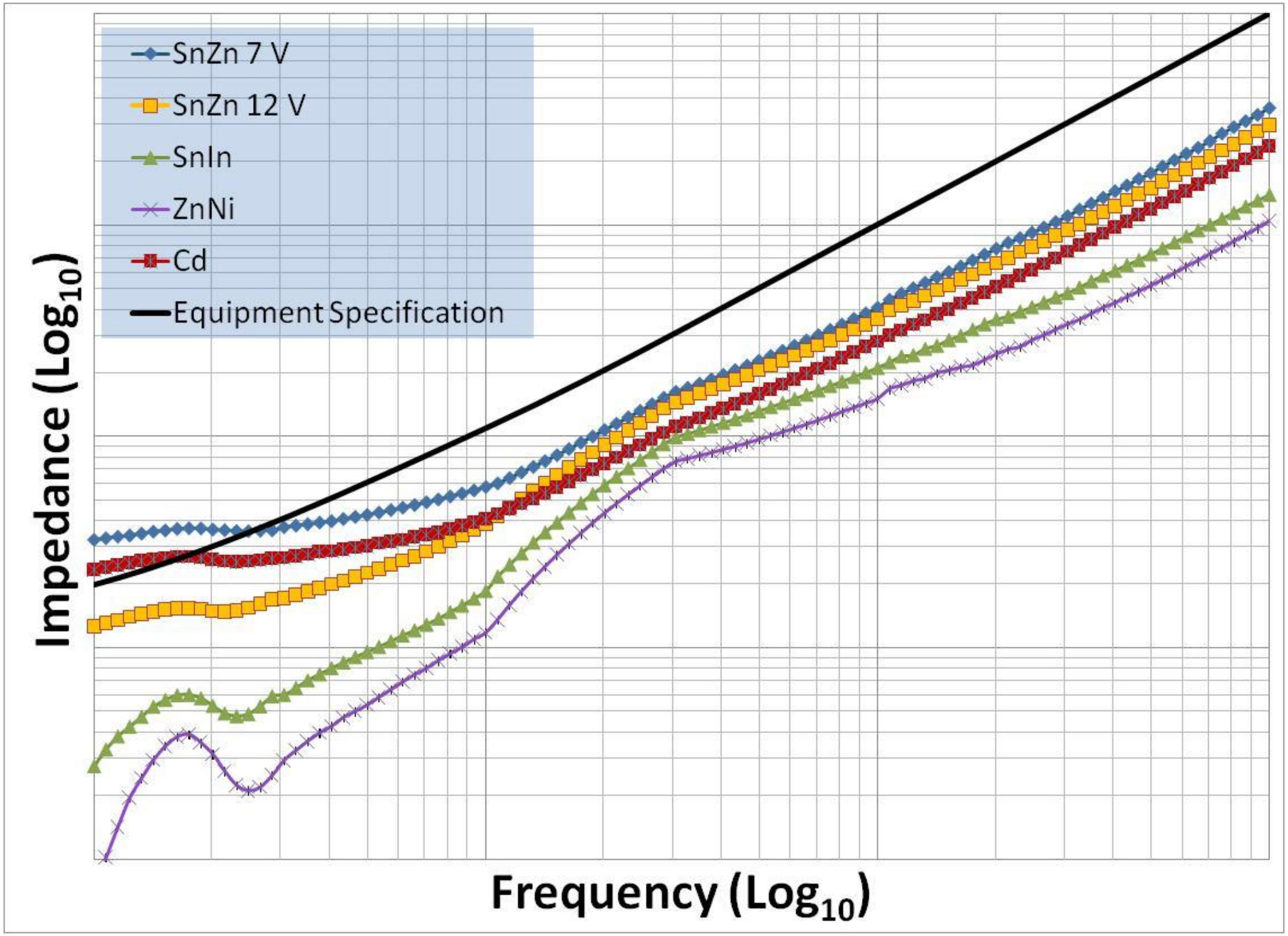
To 4-Wire Low Contact Resistance Meter



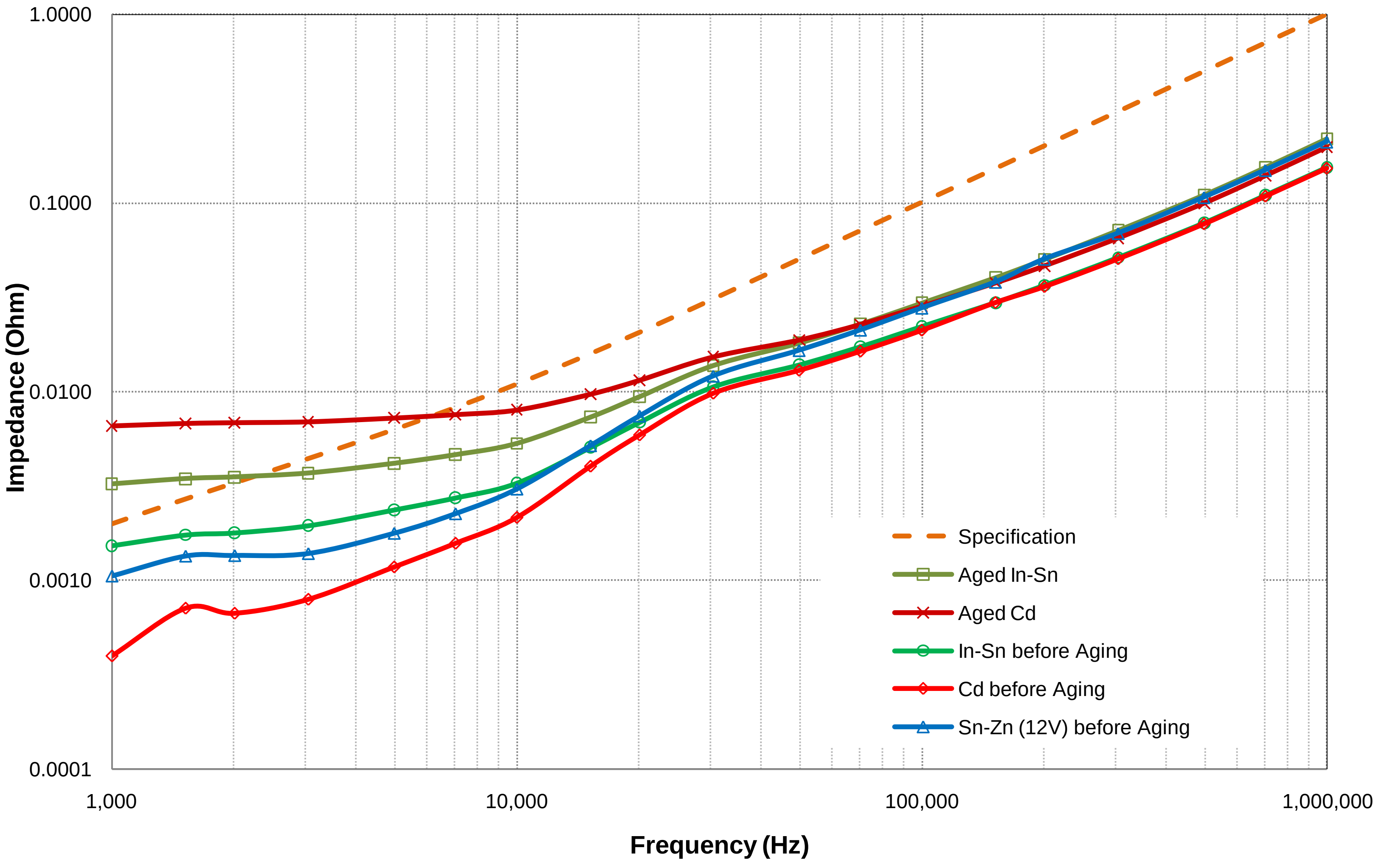
Electrical Isolation (plywood)

Test set-up follows MIL-DTL-81706

Electrical Resistance Results, Round 1



Electrical Resistance, Round 2, Aged Panels



Temperature Cycling

Table 6. Temperature Cycling Conditions for Each Test Cycle

Step Number	Temperature Condition	Temperature Range (°F)	Time (minute)
1	Cold	-70 to -65	120
2	Ambient	+72 to +87	5
3	Hot	+175 to +178	120
4	Ambient	+87 to +72	5

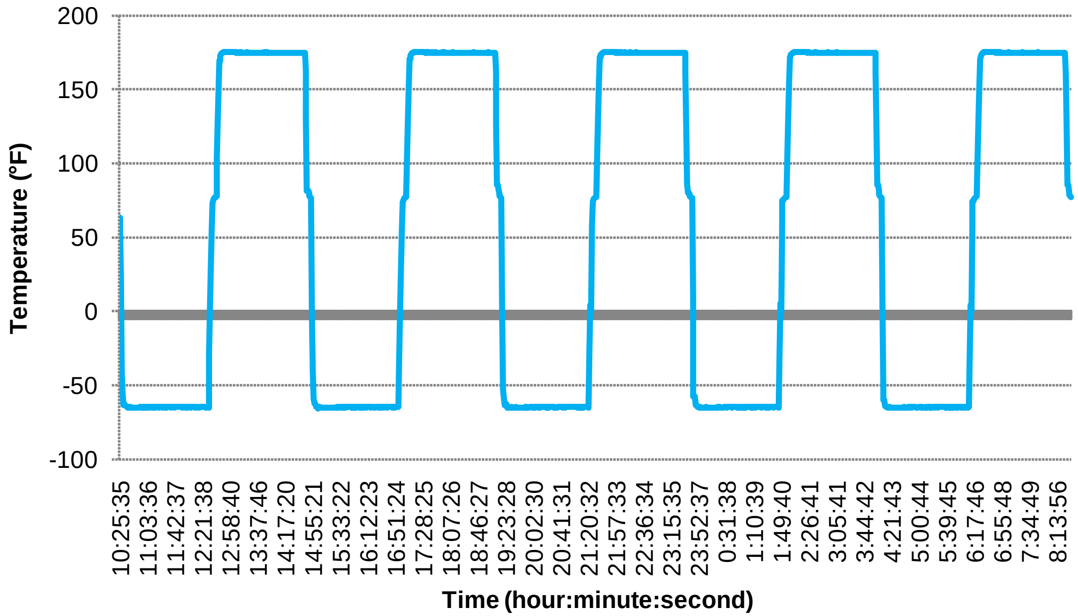
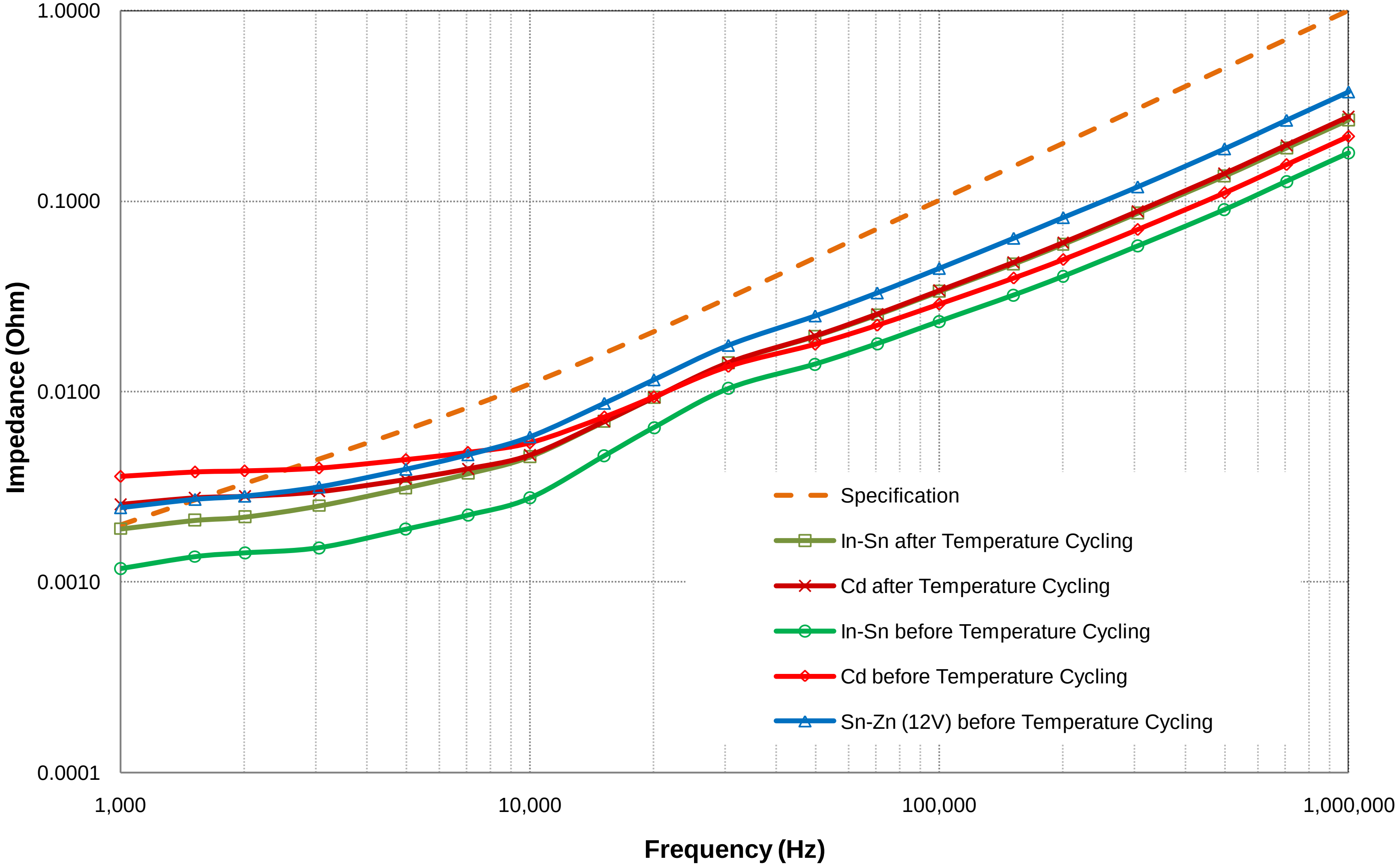


Figure 1. Variation of Temperature with Time for Temperature Cycling Test

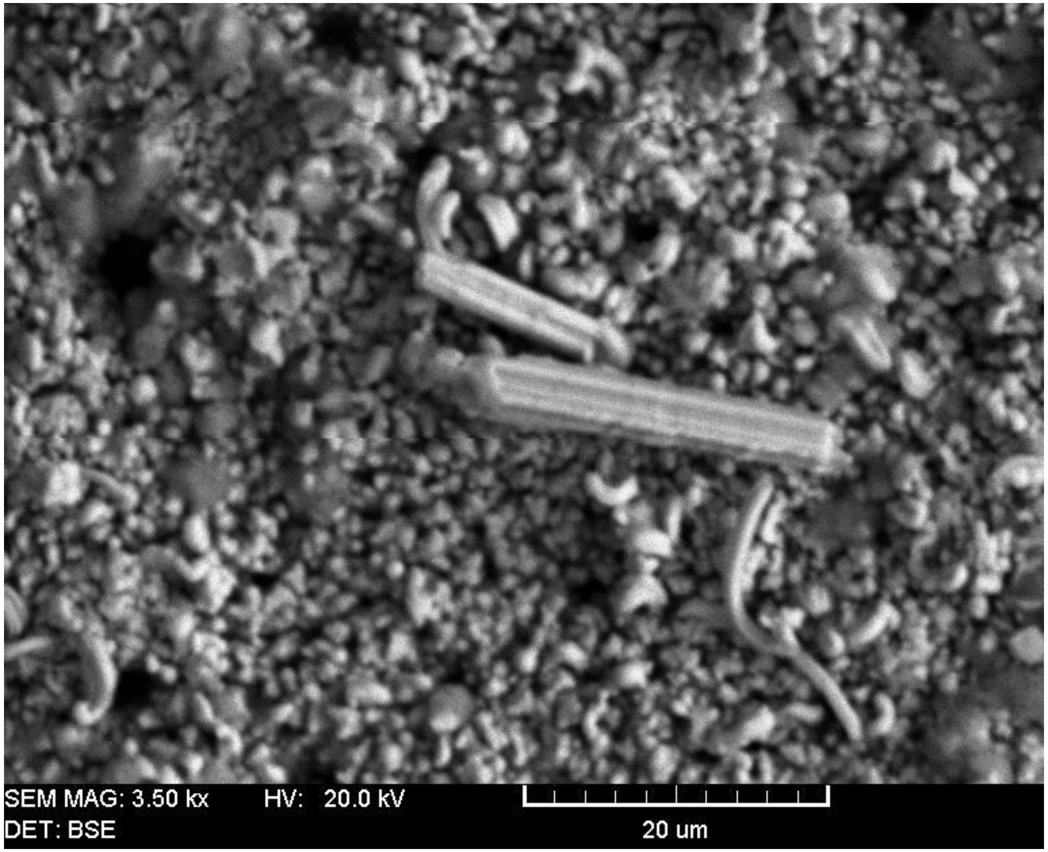
Electrical Resistance, Round 2, Temperature Cycling



Whisker Growth

One panel of tin-zinc alloy plated panels (at 12-volts processing) produced whiskers within 1,000 hours of exposure at 131°F and 85% Relative Humidity.

All other panels passed under ambient test conditions.



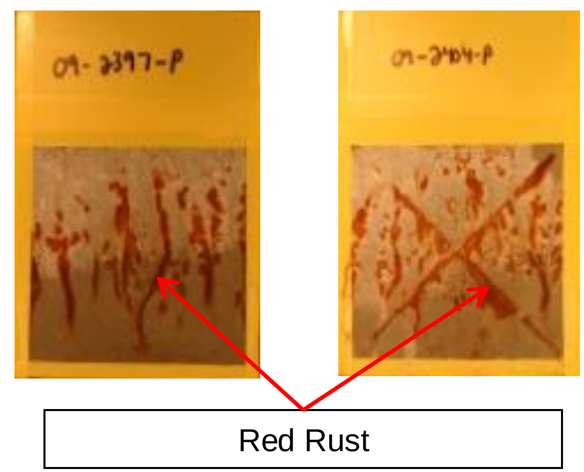
Tin whiskers on tin-zinc alloy plating. All other tin-zinc, tin-indium and zinc-nickel alloy plated panels had passed within 1,000 hours of testing.

Whisker Growth Tests Results

Whisker Observation				
Panel Type	**Baseline**	**1000 hr**	**2000 hr**	**3000 hr**
Cd, 85 ^{0}F 60%	No	No	No	No
Cd, 130 ^{0}F 85%	No	No	No	No
ZnNi, 85 ^{0}F 60%	No	No	No	No
ZnNi, 130 ^{0}F 85%	No	No	No	No
SnZn 12v 85 ^{0}F 60%	No	No	No	No
SnZn 12v 130 ^{0}F 85%	No	Yes	Yes	Yes
InSn 7030 85 ^{0}F 60%	No	No	No	No
InSn 7030 130 ^{0}F 85%	No	No	Yes	Yes

Corrosion Resistance

- **Testing per ASTM B 117**
  - 6 panels per coating
    - 4 x 6 panels
    - Both scribed and unscribed panels evaluated
- **Testing Results**
  - Cd – 3000 hrs, scribed and unscribed
  - SnZn – 24 hrs, scribed and unscribed
  - InSn – unscribed, 192 hours
  - ZniNi – did not pass bend adhesion and did not proceed to this test



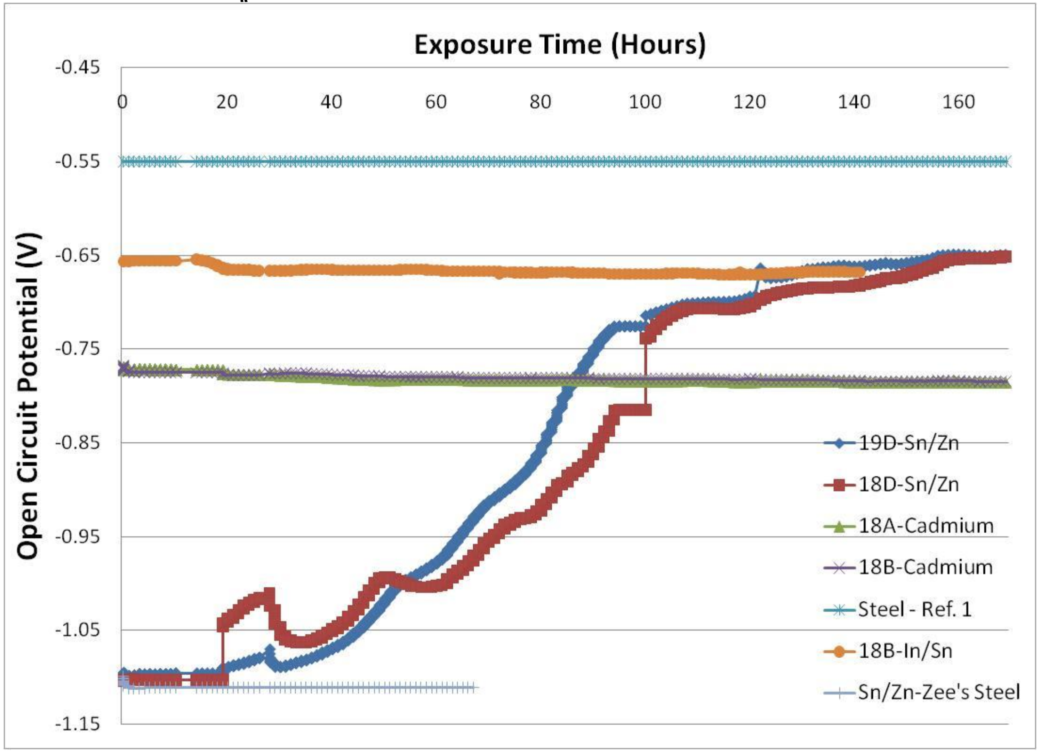
SnZn, 24 hrs exposure

Corrosion Chart

Test		Cd Coatalyte #312	Sn-Zn 12 V LDC-5030	In-Sn LDC 4901/5001
	Unscribed[2]	3 (0.61 ± 0.06)	0 (0.53 ± 0.02)	1 (0.37 ± 0.02)
Electrochemical Properties (ASTM G 3)	OCP (V)	-0.78	NSS[9]	-0.69
Via EIS Method 1	Corr Rate (mpy)	32.3 ± 29.3	5.4 ± 6.6	1.3 ± 0.02
Via EIS Method 2	Corr Rate (mpy)	32.1 ± 28.7	7.0 ± 7.0	1.5 ± 0.01
Via cathodic polarization (neutral buffer)	Corr Rate (mpy)	2.5 ± 0.07	69 ± 71	0.52 ± 0.11
Via Tafel measurements of cathodic polarization (DHS)	Corr Rate (mpy)	4.0 ± 3.8		0.31 ± 0.24
Via Tafel measurements of anodic polarization (DHS)	Corr Rate (mpy)	73 ± 104		0.60 ± 0.18
Pitting	Number	None	None	None
Crevice Corrosion	Level	Mostly Severe	Mostly Severe	None to Moderate

Electrochemical Properties
(Open Circuit Potential)

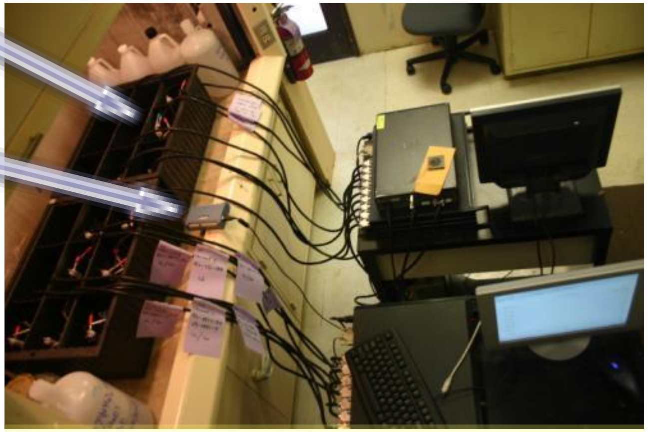
In-Sn coatings immersion exposure to the neutral solution of $Na_2SO_4 + H_3BO_3$



Open Circuit Potential Preliminary Results

Test Cells per Samples

Thermocouples



Multiplex 16 Samples

Samples vacuum storage

Test Cell for Samples

Summary

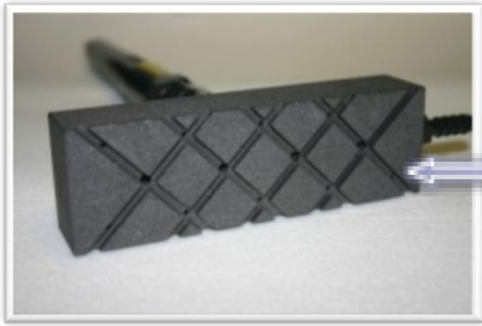
- Mission Essential Need to replacement Cadmium coating on DoD weapon system with “greener” / safer alternative(s)
- Replacement needs to be sacrificial to mild steel, and electrically conductive throughout its service – this limits the options.
- Round 1 and Round 2 tests are complete
- No candidate peformed as well as the cadmium on the corrosion resistance tests
- InSn peformed better than the cadmium in the electrical resistance tests
- Currently looking at other atlernatives.

Back Up Slides

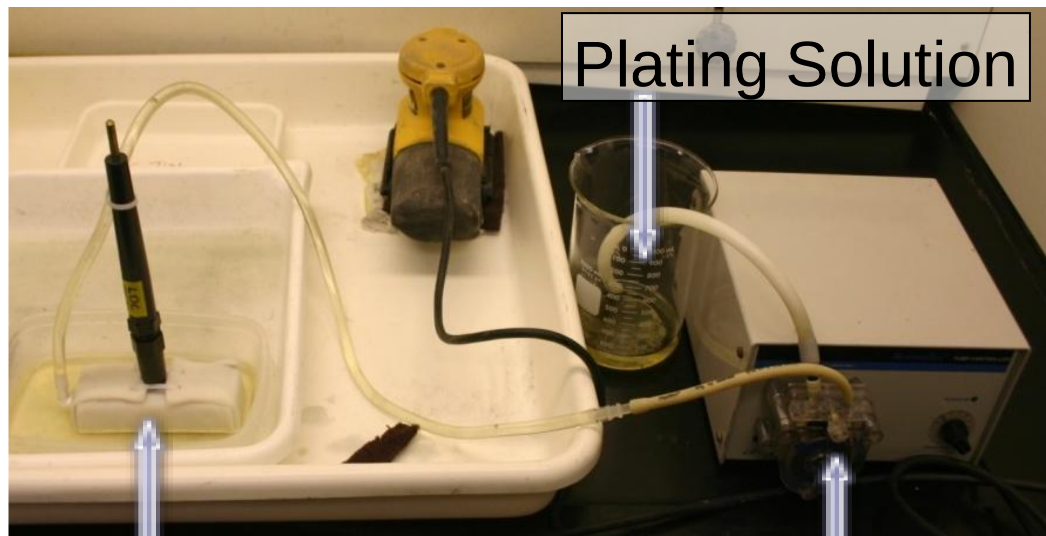
Background

- Cd has been a good coating for this weapon system.
  - Some of the mild steel component mating surfaces are electroplated with Cd
  - Prevent corrosion
    - Sacrificial to prevent formation of oxides of mild steel
    - Galvanic couple with aluminum alloys and stainless steel
  - Ensure a high electrical conductivity and sufficient grounding path during its service life
  - Provide the ability to withstand harsh weapon system environments
- Cd coating / repair process by brush plating that references SAE-AMS-QQ-P-416

Alternate Anode Arrangement



Anode Machined for Metered Chemical
(either graphite [shown] or plastic for dimensionally stable)



Test Panel

Sleeved Anode

Chemical Metering Pump

Meter chemical to anode, through its sleeve, and onto the part

Cd Spot Repair (Brush) Plating

Procedure:

1. Remove soils/corrosion from plated surfaces
2. Activate the substrate and undamaged Cd
3. Brush plate Cd onto the activated areas:
   - Wrap sacrificial Cd anode in an absorbent sleeve
   - Keep the anode sleeve wet with plating solution
   - Apply a steady, uniform anode motion on the part
   - Use a constant voltage until the target ampere-hour is reached
4. Inspect the Cd plating quality

Alternatives (Alts.) per QQ-P-416

1. Aluminum
2. Cadmium-titanium
3. Zinc
4. Lead
5. Zinc-cadmium
6. Nickel
7. Zinc-nickel
8. Nickel-cadmium
9. Tin
10. Tin-cadmium
11. Tin-nickel
12. Tin-zinc
13. Acrylic
14. Epoxy
15. Fluorocarbons
16. Nylon
17. Polyester
18. Polyurethane

Caveats of Indium Alloys

1. Low temperature eutectic:
   - The tin-indium system eutectic is 244°F at ~48.3 weight % tin
   - The cadmium-indium-tin system eutectic is ~199°F
   - Good for a solder
2. Greater hardness than both Cd and indium:
   - Less deformable on the mating surfaces
   - Potentially reduces the contact between these surfaces and electrical conduction
3. Relatively expensive; therefore, conduct a review of its cost/benefit to adopt indium alloy plating

Indium Alloy Brush Plating

- Start at 6 volts, adjust for target current density
  - Nominal average of 2.5 amperes/square inch
- Manage the process resistive heat, which raises the temperature of the anode and a thin panel
  - Use a thicker, ⅛- to ¼-inch thick panel
  - Convert the anode to platinum wire instead of graphite
  - Feed the plating solution through the anode to cool it
- Use a soft anode sleeve material

Indium alloy plating